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Dynamic Mass Balance of PCB (Polychlorinated Biphenyls)

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DYNAMIC MASS BALANCE OF PCB AND SUSPENDED SOLIDS IN SAGINAW BAY -- A CASE STUDY

by

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16. ABSTRACT

In Saginaw Bay, Lake Huron, about 3.7 metric tons of PCB remain in the active sediment and inputs from the Saginaw River and atmospheric deposition contribute about 1.4 kg PCB per day. In 1977 the U.S. E.P.A. initiated a research effort on Saginaw Bay which was chosen because of the existing PCB contamination, its importance as a commercial and sports fishery, and because, within a relatively small area, many of the limnological processes occurring in the Great Lakes are represented. Therefore, findings from this work might be extrapolated to other parts of the Great Lakes or other similar water systems.

This paper presents an analysis of conditions in the bay during 1979 and a projection of future conditions using a dynamic mass balance model. The primary research questions addressed are: 1) whether simulation models of "total PCB" are sufficiently accurate or whether refined models considering at least mixtures are necessary, 2) whether volatilization of PCB is occurring, and 3) what is the expected longevity of PCB in the system.

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DYNAMIC MASS BALANCE OF PCB AND SUSPENDED SOLIDS IN SAGINAW BAY — A CASE STUDY

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INTRODUCTION

Although regulations have reduced their use and eliminated their manufacture in the U.S., polychlorinated biphenyls (PCBs) remain a serious environmental issue. Particularly in the Great Lakes from which large quantities of fish are caught for human consumption, the PCB question remains, "How long will PCB concentrations in some fish remain above the FDA action limit of 5 mg/kg?" Data collected by various agencies on PCB levels in Lake Michigan fish have revealed a decreasing trend since 1972 [1], but it is apparent that an extended period of time will be required for levels to decline below the FDA limits for some species [2]. Evidently, reservoirs of PCB remain in the environment which continue to act as sources of contamination to the Great Lakes. Continuing sources include landfills, road pavements previously sealed with PCB oil mixtures, contaminated sediments in harbors and bays and long-range atmospheric trans-

port and deposition. Specific questions remain concerning the additional effort required to locate sources and decontaminate or seal these reservoirs. Problem areas include the contaminated sediments of Waukegan Harbor, the Kalamazoo river estuary on Lake Michigan, Raisin River, and the Saginaw River and its tributaries.

To assist in answering regulatory questions, research and surveillance data are needed to evaluate the relative importance of the existing inputs, sediment reservoirs, and the processes controlling transport and fate and exposure. In Saginaw Bay, Lake Huron, about 3.7 metric tons of PCB remain in the active sediment and inputs from the Saginaw River and atmospheric deposition contribute about 1.4 kg PCB per day. In 1977 the U.S. E.P.A. initiated a research effort on Saginaw Bay which was chosen because of the existing PCB contamination, its importance as a commercial and sports fishery, and because, within a relatively small area, many of the limnological processes occurring in the Great Lakes are represented. Therefore, findings from this work might be extrapolated to other parts of the Great Lakes or other similar water systems.

This paper presents an analysis of conditions in the bay during 1979 and a projection of future conditions using a dynamic mass balance model. The primary research questions addressed are: 1) whether simulation models of "total PCB" are sufficiently accurate or whether refined models considering at least mixtures are necessary, 2) whether volatilization of PCB is occurring, and 3) what is the expected longevity of PCB in the system.

DATA BASE DEVELOPMENT

The present research focuses on the 1979 surveys of Saginaw Bay. In 1979 ten cruises lasting about one week each were conducted and samples collected at 26 stations at one meter and one meter above the bottom (see Figure 1). Samples were serially filtered on-board to obtain subsamples for particulate fractions: 1) 0.7 to 37 μm; 2) 37 to 74 μm; 3) 74 to 210 μm; 4) 210 to 1000 μm. The dissolved fraction is operationally defined as the filtrate or portion of the sample containing solids $\leq$ 0.7 μm. On-board analyses included temperature, conductivity, pH, Secchi depth, and turbidity. Samples were analyzed later for suspended solids and PCB. PCB analyses were made using a dual column Hewlett-Packard gas chromatograph fitted with an auto sampler and electron capture detector and an Aroclor 1242-1260 standard. PCB results were reported in terms of total PCB, Aroclor 1242, Aroclor 1260, and in terms of six homo-

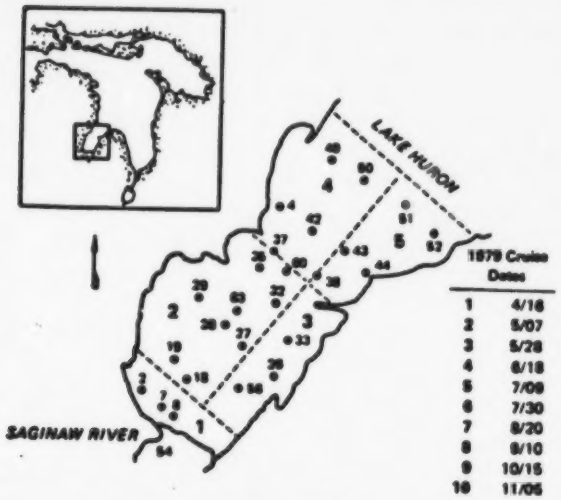


Figure 1. Saginaw Bay 1979 sampling network and segmentation.

logs (2 to 7 chlorines/biphenyl molecule) based on Sawyer [3]. Each sample collected was characterized by up to 45 PCB/solid fraction combinations. Details of the sampling procedures and PCB analyses are described by Smith et al. [4]. Although there continues to be much discussion about the accuracy of PCB analysis techniques, and fish samples analyzed by packed column GC have been as high as a factor of two higher than duplicate samples analyzed using capillary column GC [5], the data are relatively consistent. This is an important consideration in using the data for modeling. In the future the absolute levels of PCB reported herein may have to be adjusted as indicated by comparisons of packed column and capillary results.

DATA ANALYSIS

For the purpose of the data presentation, as well as for modeling, the data were stratified according to five segments shown in Figure 1 with Saginaw River represented by one station, SB0054. In addition, for this presentation the individual particulate fractions have been summed and the total particulate data ($\geq$ 0.7 μm) presented. Only the data for total PCB (TPCB), Aroclor 1242 (A1242) and Aroclor 1260 (A1260) are presented. In all cases TPCB is the sum of A1242 and A1260. In addition only those samples where all

data for dissolved and total particulate were available are used. Total PCB concentrations were calculated for each sample by the addition of the dissolved and total particulate.

A summary of the data is presented in Tables I-III. Averages for all data by segment, TPCB, A1242, A1260, (total, particulate, and dissolved) and suspended solids are presented. In these tables the distribution coefficients presented were calculated from the average data by Equation (1):

$$K_p = \frac{C_p/S}{C_D} \qquad (1)$$

	Units
K_p = distribution coefficient	(ℓ-mg^{-1})
C_p = particulate PCB concentration	(ng-ℓ^{-1})
C_D = dissolved PCB concentration	(ng-ℓ^{-1})
S = suspended solids concentration	(mg-ℓ^{-1})

As shown in Figure 2, concentrations of TPCB, A1242, and A1260 decrease from Saginaw River to Lake Huron. This could be due to simple dilution as well as losses via settling or volatilization. It is evident that A1242 is predominant in the river with an average concentration of about 130 ng/ℓ compared to 45 ng/ℓ for A1260; whereas, in the bay the concentrations of each mixture are almost identical, although A1260 is higher in the outer bay (Figure 3). This implies that whatever mechanisms are involved they are different for each of the mixtures.

For both mixtures the particulate fraction dominates in the river whereas the dissolved fraction becomes more dominant from the inner bay to Lake Huron, as indicated in Figure 3. This follows the pattern of higher solids concentrations in the river than in the bay and implies the importance of solids/PCB relationships. This is further explained in Figure 4 where K_p's as calculated from the data using Equation (1) are shown. Generally, K_p's for A1242 are lower than those for A1260 and, for both mixtures, K_p's are lower in the river and in the shallower segments, 1 and 3. This may be due to the higher proportion of sands and clays due to transport and resuspension than in the deeper segments where the lighter, organic and detrital matter predominate.

Finally, Figure 5 shows the temporal relationships of chloride, suspended solids, and fractions of mixtures of PCB for segment 2. Particulate PCBs track with suspended solids with lower concentrations in the summer. In contrast, the

Table I. Average Total PCB and Suspended Solids in Saginaw Bay, 1979

Segment		Total PCB			Sus. Sol. mg/ℓ	Mass PCB/ solids ng/mg	Distribution Coefficient ℓ/kg
		Total ng/ℓ	Dissolved ng/ℓ	Particulate ng/ℓ			
1	$\bar{x}$	43.1	27.0	16.2	15.2	1.065	39473
	S_d	20.2	22.0	6.04	3.96		
	S_e	6.09	6.62	1.82	1.06		
	N	11	11	11	14		
2	$\bar{x}$	26.4	14.8	11.6	9.68	1.2	80970
	S_d	11.5	9.47	7.95	5.73		
	S_e	1.69	1.40	1.17	0.906		
	N	6	46	46	30		
3	$\bar{x}$	5.6	15.7	9.91	12.2	0.81	51738
	S_d	24.4	21.4	4.43	5.72		
	S_e	6.09	5.36	1.11	1.65		
	N	16.0	16	16	12		
4	$\bar{x}$	18.1	14.1	3.98	3.03	1.31	93160
	S_d	10.2	10.2	2.24	1.94		
	S_e	1.96	1.97	0.469	0.389		
	N	27	27	27	25		
5	$\bar{x}$	6.2	13.7	2.57	2.65	0.970	70789
	S_d	14.7	15.2	1.32	2.57		
	S_e	3.47	3.59	0.312	0.624		
	N	18	18	18	17		

Table II. Average Aroclor 1242 and Suspended Solids Concentrations in Saginaw Bay, 1979

Segment		Aroclor 1242 Total ng/ℓ	Dissolved ng/ℓ	Particulate ng/ℓ	Sus. Sol. mg/ℓ	Mass PCB/ solids ng/mg	Distribution Coefficient ℓ/kg
1	$\bar{x}$	23	15.67	7.45	15.2	0.490	31420
	S_d	12.6	12.3	2.36	3.96		
	S_e	3.80	3.72	0.712	1.06		
	N	11	11	11	14		
2	$\bar{x}$	13.4	8.09	5.31	9.68	0.549	67806
	S_d	7.81	6.51	3.79	5.73		
	S_e	1.15	9.959	0.558	0.906		
	N	46	46	46	40		
3	$\bar{x}$	12.7	8.13	4.52	12.2	0.370	45571
	S_d	13.2	11.3	2.48	5.72		
	S_e	3.31	2.83	0.621	1.65		
	N	16	16	16	12.00		
4	$\bar{x}$	7.66	5.95	1.71	3.03	0.564	94850
	S_d	3.87	3.79	1.20	1.94		
	S_e	0.745	0.730	0.231	0.389		
	N	27	27	27	25		
5	$\bar{x}$	6.87	5.83	1.04	2.65	0.392	67316
	S_d	7.07	7.23	0.515			
	S_e	1.67	1.70	0.121			
	N	18	18	18			

Table III. Average Aroclor 1260 and Suspended Solids Concentrations in Saginaw Bay, 1979

Segment		Aroclor 1260 Total ng/ℓ	Aroclor 1260 Dissolved ng/ℓ	Aroclor 1260 Particulate ng/ℓ	Sus. Sol. mg/ℓ	Mass PCB/ solids ng/mg	Distribution Coefficient ℓ/kg
1	$\bar{x}$	20.1	11.4	8.70	15.2	0.572	50208
	S_d	8.59	10.4	4.12	3.96		
	S_e	2.59	3.14	1.24	1.06		
	N	11	11	11	14		
2	$\bar{x}$	13.02	6.68	6.34	9.68	0.655	98048
	S_d	11.5	5.49	4.33			
	S_e	1.69	0.81	0.64			
	N	46	46	46			
3	$\bar{x}$	12.8	7.45	5.39	12.2	0.442	59302
	S_d	11.5	10.5	2.3			
	S_e	2.88	2.64	0.57			
	N	16	16	16			
4	$\bar{x}$	10.4	8.13	2.27	3.03	0.749	92149
	S_d	7.54	7.62	1.29			
	S_e	1.45	1.47	0.249			
	N	27	27	27			
5	$\bar{x}$	9.36	7.83	1.53	2.65	0.577	73736
	S_d	8.26	8.58	0.896			
	S_e	1.95	2.02	0.211			
	N	18	18	18			

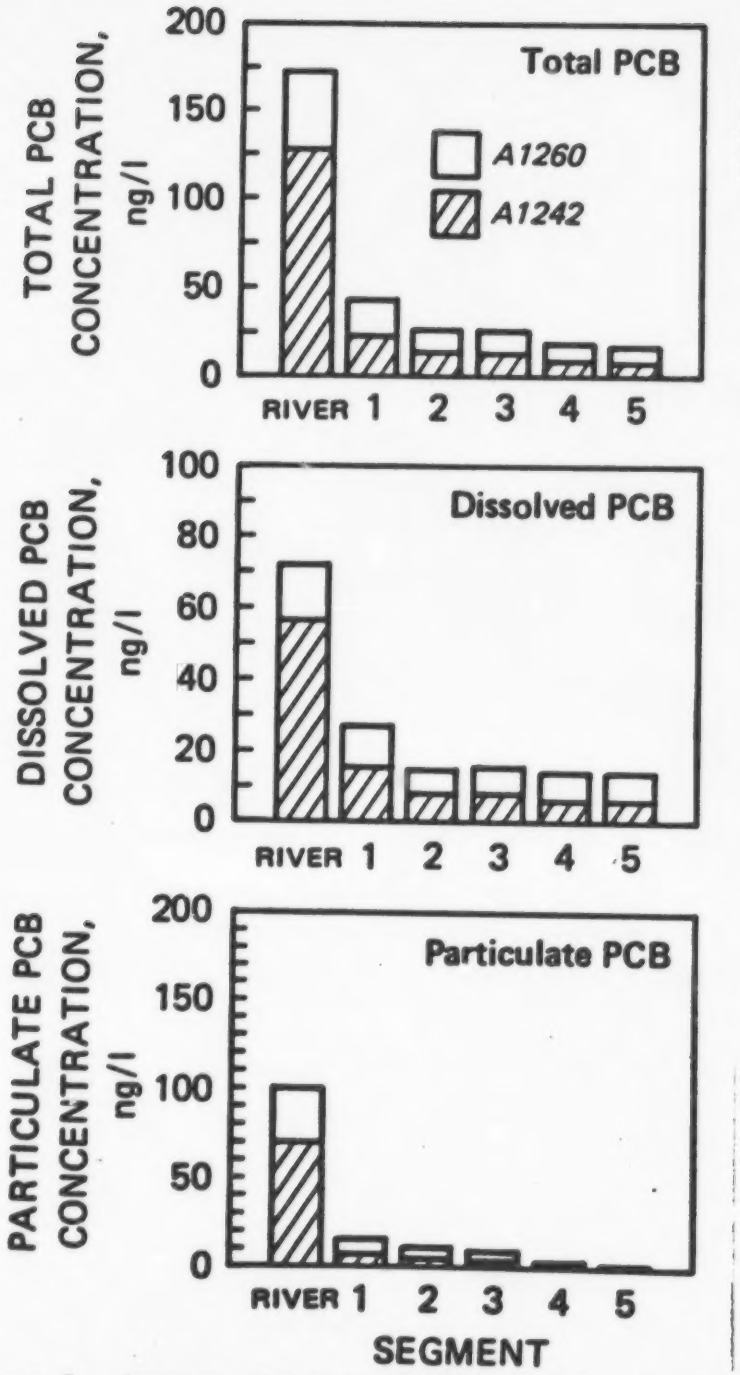


Figure 2. Average of total PCB concentrations by particulate and dissolved fractions, Saginaw River and 5 segments of Saginaw Bay, 1979.

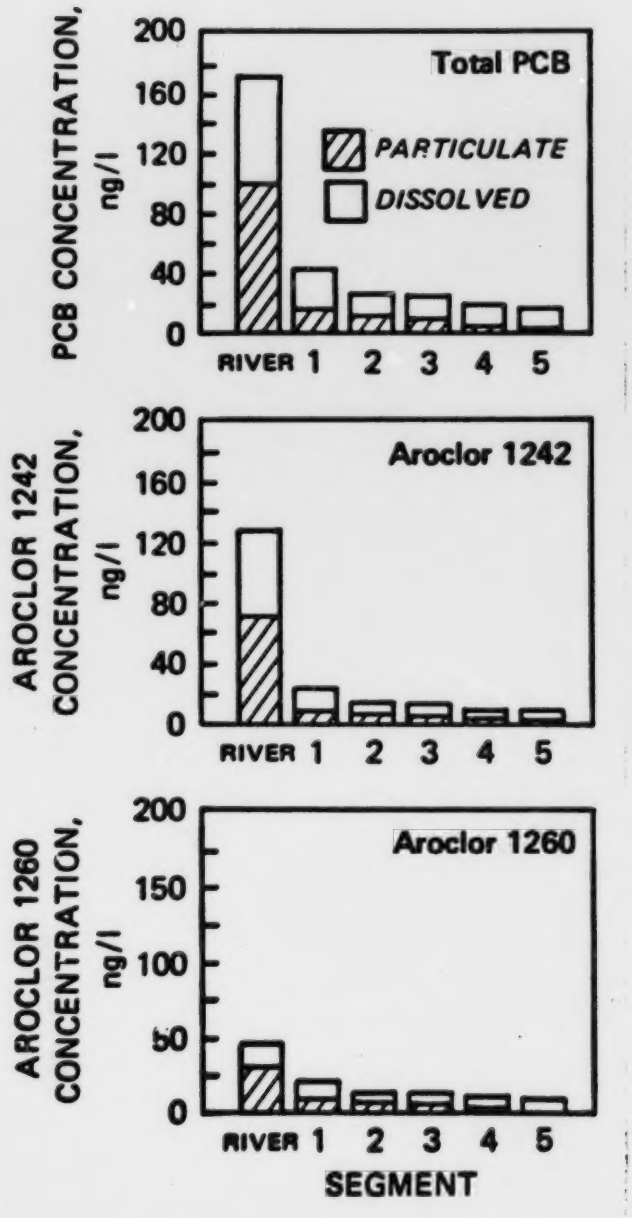


Figure 3. Average Aroclor 1242 and Aroclor 1260 concentrations in Saginaw River and 5 segments of Saginaw Bay.

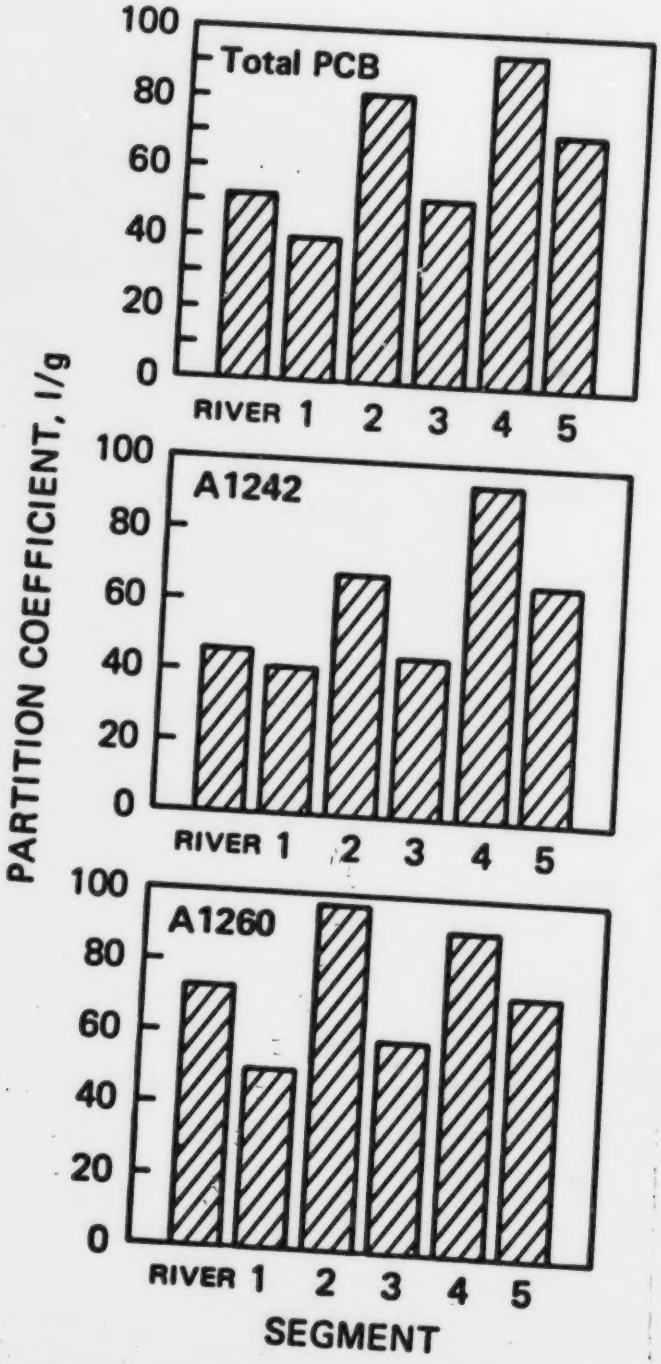


Figure 4. Distribution (partition) coefficients for total PCB, Aroclor 1242 and Aroclor 1260 in Saginaw Bay, 1979.

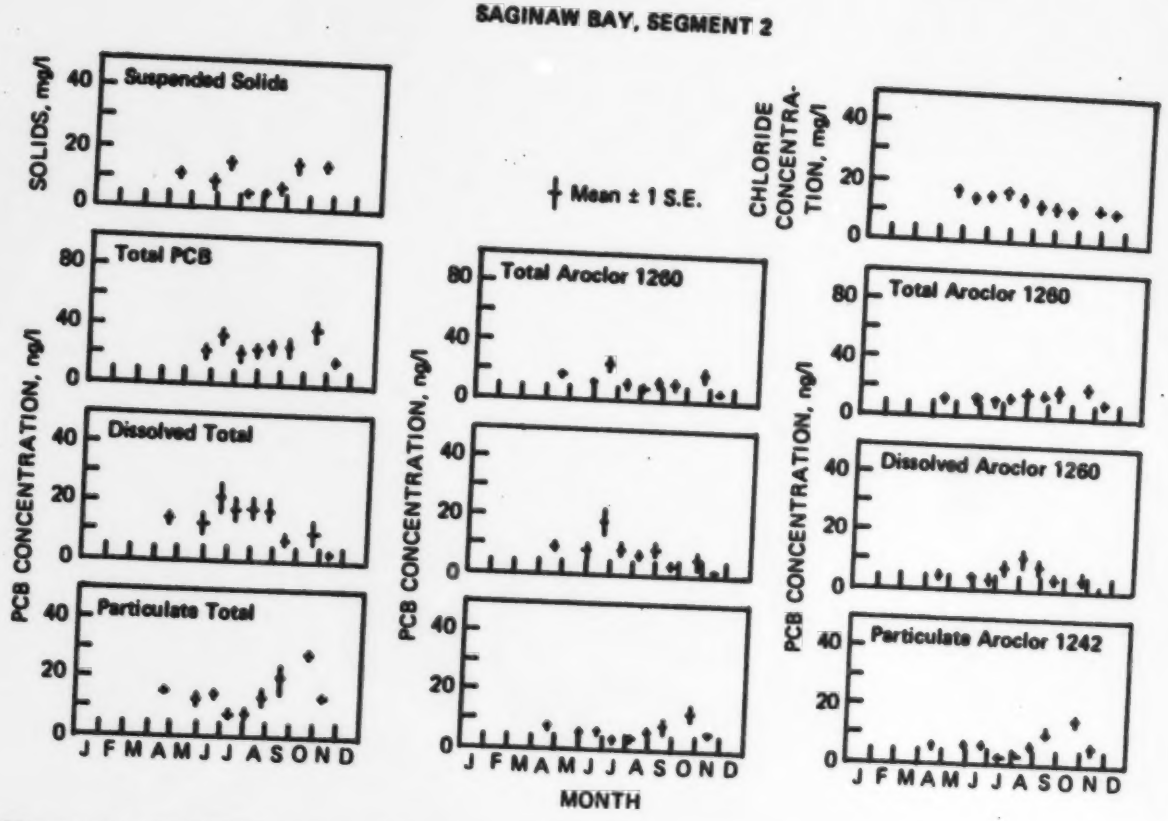


Figure 5. Cruise average PCB, suspended solids and chloride concentrations in Saginaw Bay, segment 2, 1979.

dissolved fraction is higher during the summer. This could be due to just the higher inputs in the spring and fall, or seasonality in some of the kinetic processes, or a combination of these.

Many inferences about cause and effect may be made by inspecting the data, however, because of the complex nature of PCB transport and kinetics it is difficult to discern the relative importance of each without the aid of a deterministic, dynamic mathematical model.

MODEL DEVELOPMENT

The data analysis reveals several possible factors that should be included in a modeling framework. For example, it appears necessary to include the relationship of PCB with suspended solids which requires formulation of settling-resuspension dynamics related to wind and waves. The data also indicate that PCB should be modeled at least at the resolution of PCB mixtures rather than as total PCB. In addition, particulate and dissolved fractions must be calculated and tracked separately as specific processes like volatilization affect the dissolved fraction and settling and resuspension affect the particulate fraction. It is well known that PCBs are mixtures of large numbers of compounds [6], and further that TPCB and particular mixtures do not have a "true" Henrys law constants (H) but rather have "apparent" H's. Similarly, TPCB and mixtures do not have true distribution coefficients, bioconcentration factors, solubilities, boiling points, or other physical properties that can be determined in the laboratory and applied directly in a model. It becomes apparent that to accurately predict the transport and fate of PCB, single isomers would have to be modeled and summed to determine longevity of total PCB. Since 209 isomers of PCB are possible [7], this would be an overwhelming task for a modeler, and would push the chemical analytical capabilities of any laboratory beyond its limit.

As a refinement, however, a model for two industrial mixtures, A1242 and A1260 has been developed and calibrated to field data. The sum of these two mixtures is TPCB. This derived total is compared to the originally calibrated total PCB model and differences noted. A model for total PCB in Saginaw Bay has been developed and simulations compared to 1977 data [8] and to 1979 data [9].

The mass balance framework shown in Figure 6 is similar to that developed by Thomann [10] with the addition that PCB is represented by the two, noncoupled compartments for A1242 and A1260. The framework includes:

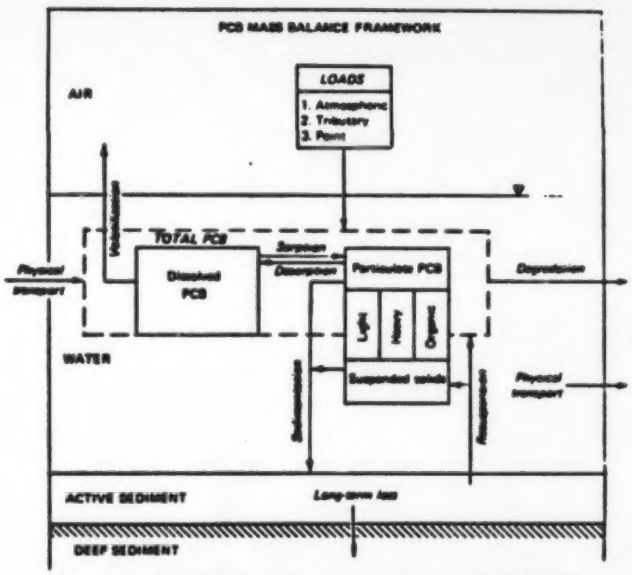


Figure 6. PCB mass balance framework.

1. Input of suspended solids and Aroclor mixtures from tributaries and the atmosphere. Solids also originate from shoreline erosion and primary production.

2. Transport of solids, PCB adsorbed to solids and dissolved PCBs within the water column and to and from Lake Huron (boundary conditions specified at Lake Huron).

3. Settling and resuspension of solids and associated particulate PCBs to and from active sediments as a function of wind, depth of water, and sediment type.

4. Long-term burial of PCB to deep sediments.

5. Volatilization of dissolved PCBs.

The underlying assumptions of the model include:

1. Adsorption-desorption of PCBs associated with solids occurs at a rapid rate relative to other processes in the system, i.e., transport and settling-resuspension so a local equilibrium assumption can be applied [10]. This allows the calculation of the particulate and dissolved fractions from total concentrations using a partition coefficient.

2. Each physical water and sediment segment is considered homogeneous and can be represented by average concentrations of solids and PCBs.

3. The horizontal movement of the active sediment layer is small relative to the water transport and can be assumed to be zero.

4. No biodegradation, photolysis, or hydrolysis of PCBs.

The modeling process applied to Saginaw Bay has progressed in the following sequence:

1. Determine the transport characateristics of the bay in 1979 by modeling chloride as a tracer substance.

2. Model solids relating bottom sediment to water concentration through an empirically derived and calibrated formulation. Solids are modeled as three types--heavy, light, and organic (originating from primary production).

3. Model the two mixtures of PCB coupled to suspended solids. Calibrate the model by adjusting the distribution coefficients until a reasonable comparison is obtained between calculated and measured total, dissolved, and particulate PCB.

4. Simulate fate and longevity of PCB by simmulating solids and PCB mass balance over an extended period into the future (ie., about fifty years).

External Material Loadings

The key driving force is the material inputs for the state variables, chloride, solids, and the PCB mixtures. The annual loading for 1979 are summarized in Table IV. Saginaw River loadings were estimated by the product of flow and concentration. The phytoplankton contribution to the solids load was obtained by estimates of the gross phytoplankton biomass production in the bay. Atmospheric loadings of PCB were provided by Murphy [11]. For a more detailed explanation of loading estimates, see Richardson et al. [9]. The loadings are input to the model as a function of time with primary loading occurring in the spring with high runoff. The estimated monthly average PCB loadings from Saginaw River are shown in Figure 7.

Table IV. Average 1979 Loadings to Saginaw Bay (Kilograms/day) for Chloride, Suspended Solids and PCB

CHLORIDE	520000
SUSPENDED SOLIDS	
SAGINAW RIVER	351500
OTHER TRIBUTARIES	89700
SHORELINE EROSION	129000
ATMOSPHERIC	37800
PHYTOPLANKTON	473300
TOTAL	1081300

PCB

	TOTAL PCB	AROCLOR 1242	AROCLOR 1260
ATMOSPHERIC [11]	0.620	0.258	0.361
TRIBUTARY	0.758	0.494	0.264
TOTAL	1.378	0.752	0.626

The model was implemented using a computer program, "Water Analysis Simulation Program (WASP)" [12], and applied to Saginaw Bay. The bay was subdivided into 19 segments (5 water and 14 sediment) as shown in Figure 8.

Physical Transport

Chloride was used as a transport tracer using the mass balance equation

$$V_k \frac{dC_k}{dt} = \Sigma W_{ck} + \sum_j Q_{jk} C_j - \sum_j Q_{kj} C_k + \sum_j E'_{jk} (C_j - C_k) \qquad (2)$$

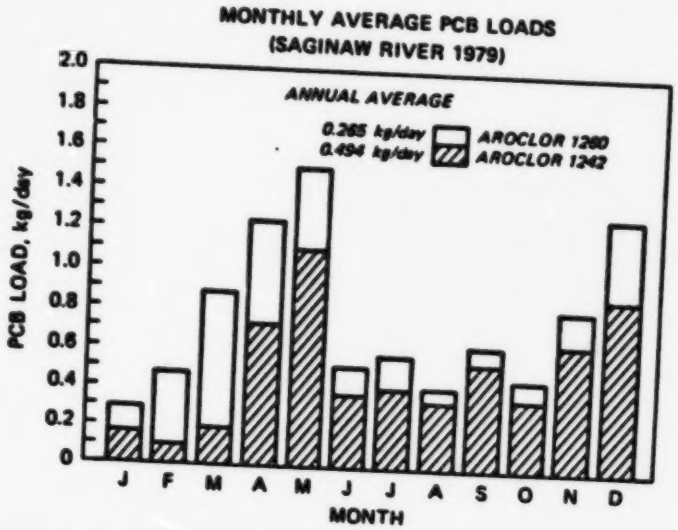
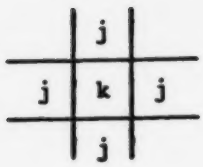


Figure 7. Monthly average PCB loads by mixture from Saginaw River, 1979.

Figure 8. Segmentation for Saginaw Bay solids/PCB model.



k = segment of interest

j = adjacent, interacting segments

where:

		Units
k	= water segment considered	
j	= adjacent water segments	
V_k	= volume of segments	(L^3)
C_k	= concentration of chloride	$(M\ L^{-3})$
t	= time	(T)
W	= input load of substance, chloride	$(M\ T^{-1})$
Q	= advective transport coefficient	$(L^3\ T^{-1})$
E'_{jk}	= dispersive transport coefficient	$(L^3\ T^{-1})$

The water transport parameters Q and E' (Equation 2) were obtained through an iterative process described by Richardson [13] whereby chloride is used as a tracer substance and values of E' and Q were selected so that the calculated concentration "fits" those measured. The final calibration of computed versus measured concentrations is shown in Figure 9.

Solids

The solids submodel includes three categories of solids: 1) light; 2) heavy; 3) organic, following the formulation of Thomann (10). Light solids include inorganic, clay fractions and detrital materials of terrestrial origin; heavy solids include non-cohesive particles, particularly sand originating from runoff and shoreline erosion; and organic solids are materials of aquatic origin including gross phytoplankton and zooplankton production. For a more detailed description of the solids model and associated data, see Richardson [9]. A summary of the solids-related model coefficients is given in Table V.

For solids the mass balance equation is

$$V_k \frac{dS_{ki}}{dt} = \Sigma W_{ski} + \sum_j Q_{jk} S_{ji} - \sum_j Q_{kj} S_{ki}$$

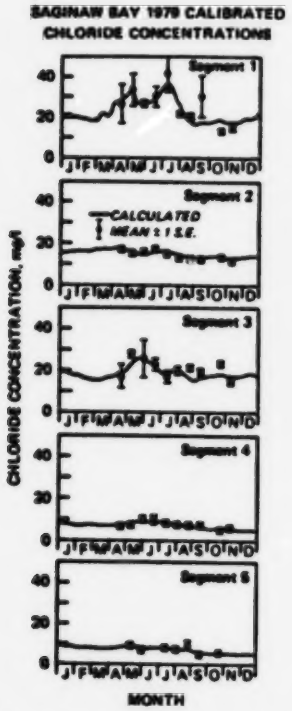


Figure 9. Calibrated chloride concentrations in Saginaw Bay, 1979.

$$+ \sum_j E'_{kj} (S_{ji} - S_{ki}) \pm \frac{S_{vi} V_k S_{ki}}{D_k} \pm R_{ski} \qquad (3)$$

where:

		Units
S_{ki}	= concentration of solids type i	$(M L^{-3})$
D_k	= average depth of segment k	(L)
S_{vi}	= gross turbulent settling velocity for solids type i	$(L T^{-1})$

$$R_{ski} = \frac{R_{vi} S_{ki} V_{sk}}{D_{sk}} \times W_f \times WRS_k \qquad (4)$$

R_{ski}	= mass resuspended for solids type i	$(M T^{-1})$
R_{vi}	= resuspension velocity for solids type i	$(L T^{-1})$

Table IV. Solids Submodel Coefficients and Variables

Description	Value	Units
Load for "light" solids (average annual)	469,000	$kg\text{-}day^{-1}$
Load for "heavy" solids (average annual)	122,000	$kg\text{-}day^{-1}$
Load for "organic" solids (average annual)	474,260	$kg\text{-}day^{-1}$
Settling velocity of "light" solids in water column	0.2	$m\text{-}day^{-1}$
Settling velocity of "light" solids in sediment layers	0.24×10^{-4}	$m\text{-}day^{-1}$
Settling velocity of "heavy" solids in water column	1.5	$m\text{-}day^{-1}$
Settling velocity of "heavy" solids in sediment layers	0.88×10^{-5}	$m\text{-}day^{-1}$
Settling velocity of "organic" solids in water column	0.1	$m\text{-}day^{-1}$
Settling velocity of "organic" solids in sediment layers	82×10^{-5}	$m\text{-}day^{-1}$
Resuspension velocity for "light" solids from active sediment	0.005	$m\text{-}day^{-1}$
Resuspension velocity for "heavy" solids from active sediment	0.000001	$m\text{-}day^{-1}$
Resuspension velocity for "organic" solids from active sediment	0.008	$m\text{-}day^{-1}$
Julian day on which ice cover disappears	74	day
Julian day on which ice cover appears appears	345	day
Wind speed below which no resuspension occurs	13	knots
Constant in resuspension/wind, Equation (5)	0.02	-
Resuspension suppression factor, Seg. 6	3	-
Resuspension suppression factor, Seg. 7	1	-
Resuspension suppression factor, Seg. 8	3	-
Resuspension suppression factor, Seg. 9	.5	-
Resuspension suppression factor, Seg. 10	.6	-
Resuspension suppression factor, Seg. 11	.35	-
Resuspension suppression factor, Seg. 12	.005	-
Resuspension suppression factor, Seg. 13	.005	-

[1]Loads input on a daily basis.
[2]No resuspension during ice cover.

D_k = depth active sediment layer (L)
WRS_k = resuspension, morphometric suppression factor

$$W_f = A\ V_w$$

$$W_f = 0 \quad \text{if } V_w \leq W_{min} \tag{5}$$

W_f = wind function
W_{min} = minimum wind velocity (L/T)
V = wind velocity (L/T)
A = constant

Total suspended solids is computed by the sum of the three sizes.

The particular empirical formulation for the solids resuspension was derived after reviewing research by Sheng [14] and Onishi [15]. These investigators have formulated detailed hydrodynamic models for sediment transport that relate wind speed and morphometry to shear stress at the sediment/water interface and subsequent resuspension. Time and space scales for these formulations are relatively small--seconds and meters--and are difficult to apply to large-scale situations such as PCB transport in Saginaw Bay. In addition, the detailed models usually consider the sediment as a boundary layer providing an infinite source of material. To answer the longevity question, a model must track mass of the sediment and sorbed PCB and simulate responses over time scales of decades.

The empirically derived formulation considers the physical factors described in the hydrodynamic models and attempts to simplify them so long-term calculations can be made. The model coefficients are determined by calibration to the suspended solids data both in the water column and sediment. The primary constraint in the long-term calculation is to maintain steady-state solids concentration in the sediment layers for each of the sediment types. The final water column calibration is given in Figure 10. Sediment solids concentrations over a 50 year period are maintained within 10% of the initial solids concentrations using 1979 wind conditions.

PCB

Two kinetic processes are assumed to predominate in the fate of PCB, adsorption-desorption and volatilization.

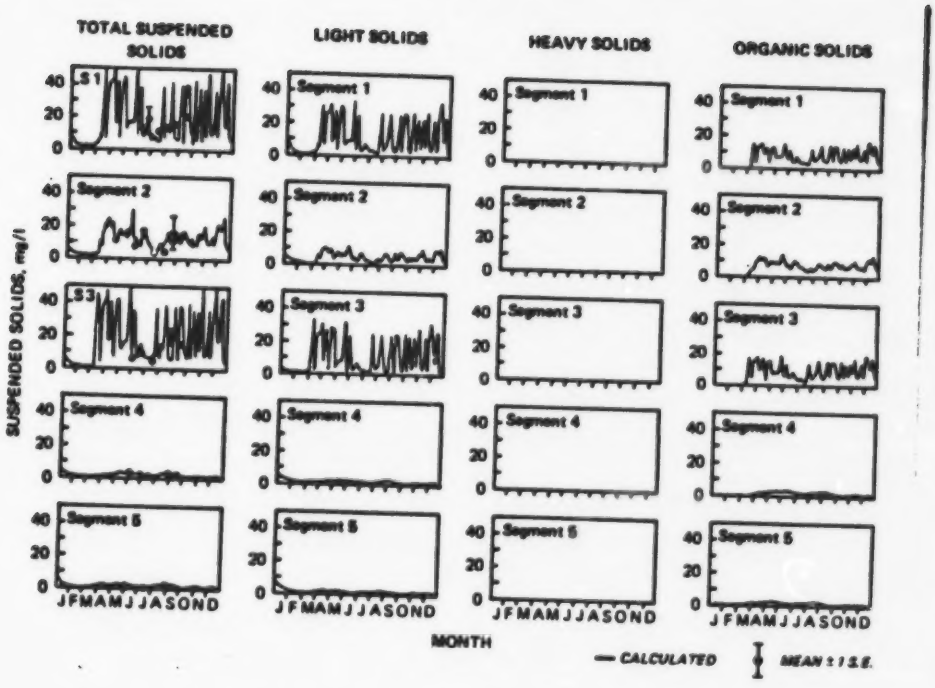


Figure 10. Calibrated suspended solids in Saginaw Bay, 1979.

Other processes affecting fate are physical transport and settling/resuspension. These processes act simultaneosly on particulate and/or dissolved fractions of each of the PCB mixtures to determine the fate of the PCB loads, attenuation in the sediments, and longevity of PCB in the system. A record of historical loadings is retained in the sediment. The sediment attenuates PCBs if they subsequently become available to the water column. If sedimentation rates are sufficient some of the PCB may become buried and permanently lost.

The PCB mass balance equation which follows the formulation of Schnoor [16] for the water column was modified by Thomann [10] and Richardson [9] to track PCB in the sediment. Further refinements to the formulation is to consider total PCBs as the sum of two mixtures, Aroclor 1242 and Aroclor 1260, which are modeled separately and added to represent total PCB.

For PCB the mass balance equation is

$$V_k \frac{dC_{Tmk}}{dt} = \sum_k W_{Tmk} \pm \sum_j T_{mjk} \qquad (6)$$

$$- \sum_{ij} \left[\frac{S_{vi}\, K_{pim}\, S_{ki}}{(1 + K_{pim}\, S_{ki})}\, C_{Tmk}\, \frac{V_k}{D_k}\right] - \sum_{ij} K_{Lm} \frac{C_{Tmk}\, V_k}{(1 + K_{pim}\, S_{ki})\, D_k}$$

$$- \sum_{ij} K_{\ell m} \frac{V_k}{D_k} \frac{(C_{Tmk}\, K_{pim}\, S_{ki})}{(1 + K_{pim}\, S_{ki})} + R_{kp}$$

where

C_{Tmk} = total Aroclor mixture, (m) concentration $(M\ L^{-3})$

T_{mjk} = net physical transport $(M\ T^{-1})$

K_{Lm} = volatilization rate (T^{-1})

K_ℓ = average loss rate for all other loss processes (T^{-1})

$$R_{kp} = \sum_i \frac{(R_{vi}\, K_{pim}\, S_{ki})}{(1 - K_{pim}\, S_{ki})}\, C_{Tkm}\, \frac{V_k}{D_k} \qquad (7)$$

$$C_{dmk} = \sum_i \frac{C_{Tmk}}{(1 + K_{pim}\, S_{ki})} \qquad (8)$$

$$C_{pmk} = \sum_i \frac{(C_{Tmk}\, K_{pmi}\, S_{ki})}{(1 + K_{pmi}\, S_k)} \qquad (9)$$

C_{dmk} = dissolved concentration for PCB mixture m $(M\ L^{-3})$

C_p = PCB, particulate concentration for PCB mixture m $(M\ L^{-3})$

$$C_T = \sum_m C_{Tm} \qquad (10)$$

C_T = total PCB (sum of all mixtures)

Great Lakes models have not yet included volatilization even though reseach by MacKay [17] and Murphy [11] have indicated its potential as a primary loss mechanism. The effective volatilization rates for A1242 and A1260 can be calculated by a method described by O'Connor [18]:

$$\frac{1}{K_L} = \frac{1}{K_\ell} + \frac{1}{K_g H} \qquad (11)$$

K_L	= volatilization rate	$(L\ T^{-1})$
K_ℓ	= liquid transfer coefficient	$(L\ T^{-1})$
K_g	= gas transfer coefficient	$(L\ T^{-1})$
H	= Henry's law constant	(dimensionless)

Henry's law constant is calculated by

$$H = \frac{p}{C_s}\ \frac{M}{T} \times 16 \qquad (12)$$

p	= vapor pressure	(mmHg)
C_s	= saturation concentration	$(mg\text{-}\ell^{-1})$
M	= molecular weight	(g/mol)
T	= absolute temperature	(K)

further,

$$K_g = \frac{D_g}{\nu_g} C_D W \qquad (13)$$

$$K_\ell = \frac{D_\ell}{\nu_\ell} C_D W \qquad (14)$$

D_g	= diffusivity of PCB in air	$(L^2\ T^{-1})$
D_ℓ	= diffusivity of PCB in water	$(L^2\ T^{-1})$
ν_g	= kinematic viscosity of air	$(L^2\ T^{-1})$
ν_ℓ	= kinematic viscosity of water	$(L^2\ T^{-1})$
C_D	= drag coefficient	(dimensionless)
W	= wind speed	$(L\ T^{-1})$

From these relationships, theoretical K_L's of 0.21 m/day meters per day and 0.17 m/day were calculated for Aroclor 1242 and Aroclor 1260, respectively. (See Table VI for values of parameters used to develop K_L). These compare

Table VI. Volatilization Parameter Values

Parameter			Aroclor 1242	Aroclor 1260
D_g	Diffusivity of PCB in air	cm^2/sec	0.04652	0.03673
D_ℓ	Diffusivity of PCB in water	cm^2/sec	5.387×10^{-6}	4.253×10^{-6}
ν_g	Kinmatic Viscosity of air	cm^2/sec	0.15	0.15
ν_ℓ	Kinmatic Viscosity of water	cm^2/sec	0.01	0.01
C_D	Drag Coefficient	-	0.001	0.001
W	Wind Speed	M/sec	5.0	5.0
p	Vapor Pressure	mm Hg	4.06×10^{-4}	4.06×10^{-5}
C_s	Saturation Concentration	mg/ℓ	0.35	0.027
M	Molecular Weight	g	261	372
T	Temperature	°K	289	289
H	Henry's Law Constant (calculated Eq. 12)	-	0.01676	0.0309

to 1.37 and 1.6 m/day estimated by MacKay [17]. As will be described below, these K_L's were used as initial estimates for volatilization but were changed during the calibrations.

RESULTS OF PCB MODELING

Model results for four basic simulations are compared in Figure 11, where the average field data are compared to the average calculated concentrations over the same period of time (April-November). Simulation A represents the total PCB model; B, the total PCB model with volatilization; C,

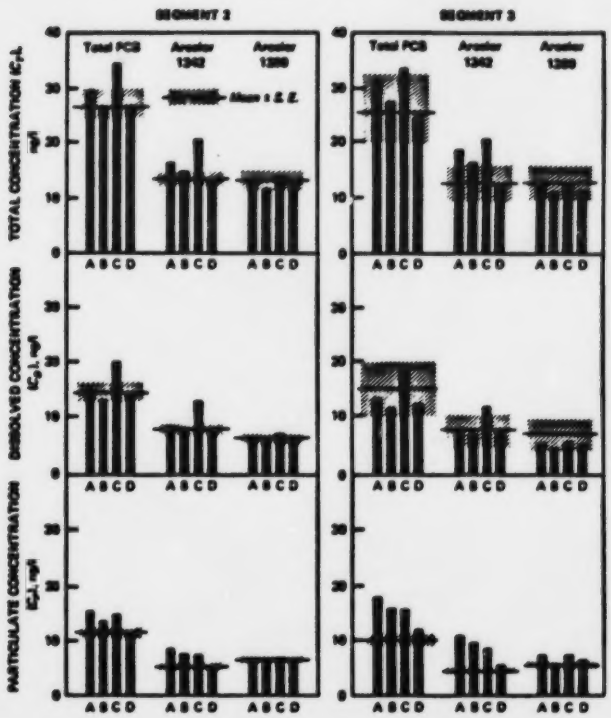


Figure 11. Comparison of average model simulations with average field data: A) Total model, no volatilization; B) Total model with volatilization; C) Two mixture model, no volatilization; D) Two mixture model with volatilization.

the two mixture model with different K_p's; and D, the two mixture model with volatilization. The K_p's and K_L's used for each simulation are summarized in Table VII.

Simulation A (Figure 11) represents the best fit possible of the total model after adjusting K_p. K_p's are constant for all water and sediment segments and for both mixtures KPH = .002 ℓ/mg, KPL = .050 ℓ/mg and KPP = .1 ℓ/mg. These values correspond approximately to those reported by Hiraizumi et al. [19]. The total PCB simulation is somewhat high for both fractions. Note that the problem appears to be with the particulate fraction of Aroclor 1242. Similarly, in segment 3 the particulate fraction for Aroclor 1242 is well above the data. Aroclor 1260 in both segments 2 and 3 are within two standard errors of the mean.

The time variable results for Simulation A is shown for segments 2 and 3 in Figure 12. PCBs over the year can be simulated reasonable well, however, it is not possible with the present formulation to simulate some of the temporal de-

Table VII. Calibration Coefficients for PCB Model Simulations

Simulation	Distribution Coefficients (ℓ/mg)						Volatilization Rates (m/day)	
	Aroclor 1242			Aroclor 1260			Aroclor 1242	Aroclor 1260
	KPL	KPH	KPP	KPL	KPH	KPP	K_L	K_L
A	0.05	0.002	0.100	0.05	0.002	0.100	0	0
B	0.05	0.002	0.100	0.05	0.002	0.100	0.08	0.08
C	0.02	0.002	0.06	0.04	0.002	0.10	0	0
D	0.02	0.002	0.06	0.04	0.002	0.10	0.20	0.05

KPL = Distribution coefficient for light solids.
KPH = Distribution coefficient for heavy solids.
KPP = Distribution coefficient for organic solids.

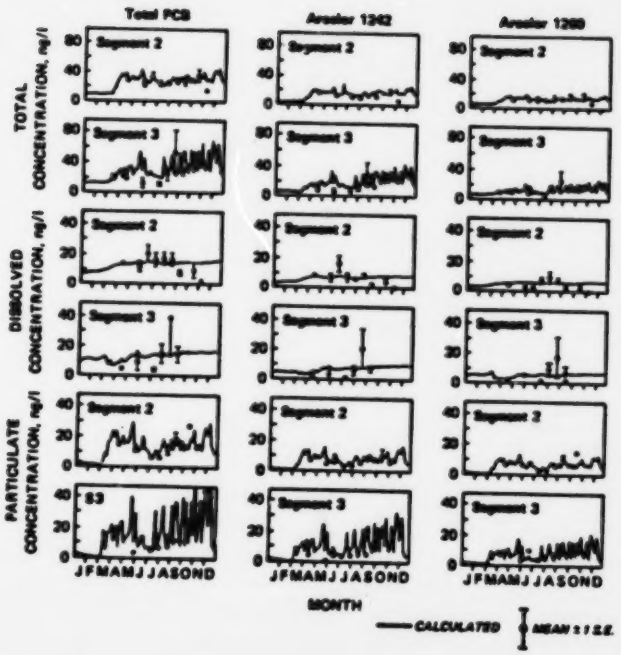


Figure 12. PCB simulation in Saginaw Bay, segment 2 and 3.

tail represented by the cruise average data. A comparison of the average of all cruise data by segment to the simulated concentrations averaged over the same period (April through November) is presented in Table VIII.

The table indicates that total PCB is simulated within 25% of the data for all segments with the best comparison in segments 1 and 2 and the worst in segments 4 and 5. Also, A1260 compares better (21%) than A1242 (38%). Also, for TPCB, A1242, and A1260 the dissolved fraction compares better than the particulate. It is also obvious that segment 2 simulations are generally more accurate than the other segments. Therefore, most of the following discussion focuses on segment 2, although segment 3 results will be shown as representative of a non-depositional segment. Segment 4 and 5 are driven primarily by the boundary concentrations and the simulations are not as accurate. This could be a result of missing loads from the outer bay tributaries, inaccurate boundary concentrations, or other phenomenon not represented by this modeling framework. However, segment 4 and 5 simulations are sufficiently accurate to provide good transition concentrations for the inner bay to Lake Huron.

Table VIII. Comparison of Computed PCB Concentrations to Average Field Data in Saginaw Bay, 1979 (Simulation A)

PCB	Segment	Concentrations (ng/ℓ) 1	2	3	4	5
Total PCB Total	Data $\bar{x}$	43.1	26.4	25.6	18.1	16.2
	S_e	(6.09)	(1.69)	(6.09)	(1.96)	(3.47)
	Model $\bar{x}$	41.7	29.6	31.1	10.8	8.4
	% Error	3.2	12.1	21.5	40.3	48.0
Dissolved	Data $\bar{x}$	27.0	14.8	15.7	14.1	13.7
	S_e	(6.62)	(1.4)	(5.36)	(1.97)	(3.59)
	Model $\bar{x}$	17.9	14.5	13.5	9.6	7.3
	% Error	33.7	2.0	14.0	31.9	96.7
Particulate	Data $\bar{x}$	16.2	11.6	9.91	3.98	2.57
	S_e	(1.82)	(1.17)	(1.11)	(.47)	(.31)
	Model $\bar{x}$	23.8	15.0	12.2	1.2	1.1
	% Error	46.9	29.3	23.2	69.8	57.0
Aroclor 1242 Total	Data $\bar{x}$	23	13.4	12.7	7.7	6.87
	S_e	(3.8)	(1.15)	(3.31)	(.75)	(1.67)
	Model $\bar{x}$	26.9	16.4	18.6	3.7	3.3
	% Error	17.0	22.3	46.4	51.9	52.0

Dissolved	Data $\bar{x}$	15.6	8.09	8.13	5.95	5.83
	Se	(3.72)	(.96)	(2.83)	(.73)	(1.70)
	Model $\bar{x}$	11.2	8.1	8.1	3.3	2.9
	% Error	28.2	0.12	0.37	44.5	50.3
Particulate	Data $\bar{x}$	7.45	5.31	4.52	1.71	1.04
	Se	(.712)	(.56)	(.62)	(.23)	(.121)
	Model $\bar{x}$	14.8	8.4	10.5	0.4	0.4
	% Error	98.7	58.1	132.0	76.6	61.5
Aroclor 1260 Total	Data $\bar{x}$	20.1	13.02	12.8	10.4	9.36
	Se		(1.69)	(2.88)	(1.45)	
	Model $\bar{x}$	15.7	13.2	12.5	7.0	5.0
	% Error	21.9	1.38	2.34	32.7	46.6
Dissolved	Data $\bar{x}$	11.4	6.68	7.45	8.13	7.83
	Se		(.81)	(2.64)	(1.47)	
	Model $\bar{x}$	6.7	6.5	5.4	6.2	4.4
	% Error	41.2	2.69	27.5	23.7	43.8
Particulate	Data $\bar{x}$	8.7	6.34	5.39	2.27	1.53
	Se		(.64)	(.57)	(.25)	
	Model $\bar{x}$	9.0	7.7	7.1	0.8	0.6
	% Error	3.44	5.67	31.7	64.8	60.8

The next simulation (B), shown in Figure 11, resulted from inclusion of a volatilization rate which was calibrated until a reasonable fit was obtained with a rate of 0.08 m/day. This results in a better comparison but with particulate A1242 remaining above the data for both segments.

Simulation C represents an attempt to reduce the particulate fraction for A1242 by adjusting the K_p's (See Table VII). The improvement in this simulation over simulation A is not with total but with particulate, especially for A1242. The difficulty is that the dissolved fraction is very sensitive in this K_p range and increases dramatically as shown in Figure 12. This results in a slightly improved particulate simulation, but with a concurrent increase in the dissolved fraction, far beyond the data, in segment 2.

It becomes clear that to calibrate A1242 the correct combination of distribution coefficients and loss rate would have to be found. To accomplish this a series of sensitivity calculations were made over a range of K_p's and K_L's. The results are shown in Figure 13, where calculated average TPCB, A1242, and A1260 for segment 2 are plotted as a function of K_L and K_p. A separate calibration for each mixture is obtained by that K_p curve which intersects the data (represented by the horizontal, dashed line) for both dissolved and particulate concentrations, at the same K_L. For A1260, that correct curve is near the curve for the K_p scale factor of 1.0 for a K_L at or near zero. For A1242 the correct combination lies between the the curves for K_p scale factors of 0.5 and 1.0, or a K_L of about 0.2 m/day and a K_p scale factor of about 0.6 (K_p's for a scale factor of 1 and those in Table VII, for Simulation A). So K_p for A1242 are about 0.6 that of A1260. This final calibration with reduced K_p's for A1242 and K_L's of 0.2 and 0.05 m/day for A1242 and A1260 are indicated by Simulation D in Figure 11. This final calibration results in an average error in segment 2 of 2.4% for TPCB, A1242, and A1260 for total, dissolved, and particulate compared to 14.9% for Simulation A (Table IX).

The mass balance for this one year simulation (D) is presented for the inner bay (segments 1, 2 and 3) in Figure 14. The magnitude of the mass transfers provide insight into the relative importance of each process. Volatilization represents the primary loss process (787 kg/yr). A mass of 312 kg/yr is transported to the outer bay (Lake Huron). Because only 398 kg are input, the difference results in a loss from the active sediment layer (717 kg/yr) and the water column (12.2 kg/yr).

If the simulation is carried out over a long period, the concentrations in the water and sediment eventually reach a new equilibrium in about 15 years. This is shown by Simulation D-1 in Figure 15. Simulation D-2 represents the pro-

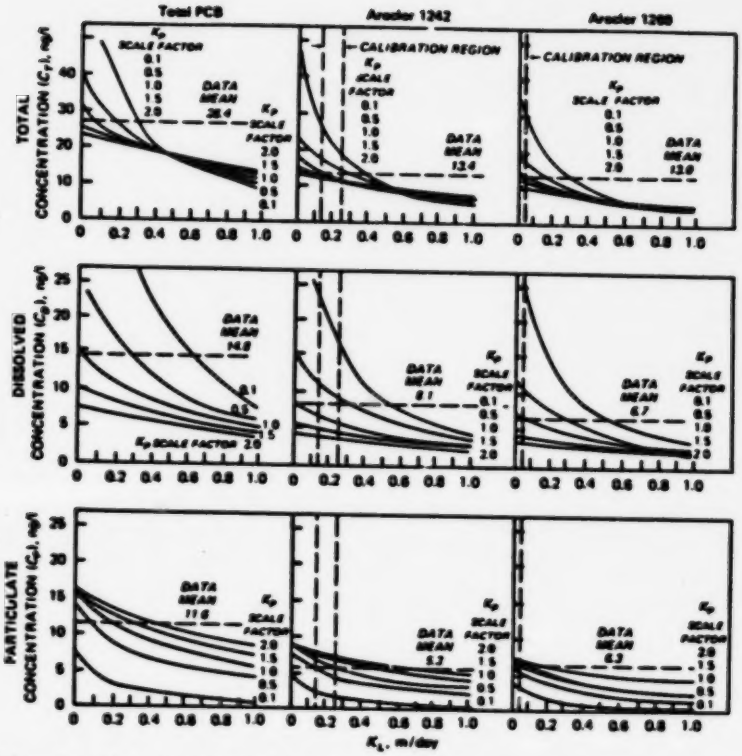


Figure 13. Sensitivity of average calculated PCB in segment 2 to volatilization rate (K_L M/day) and distribution coefficient (K_p). (See Table VII, Simulation A for K_p values at scale factor = 1).

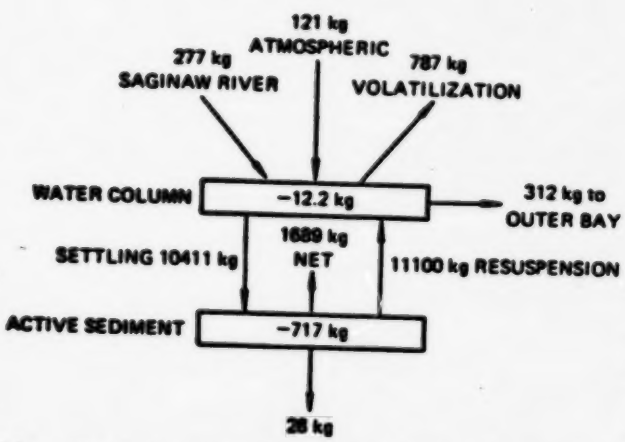


Figure 14. Mass balance for total PCB (kilograms) in inner Saginaw Bay, segments 1-3, 1979, for Simulation D.

Table IX. Comparison of Computed PCB Concentrations to Average Field Data in Saginaw Bay, 1979 (Simulation D)

PCB	Segment	Concentrations (ng/ℓ) 1	2	3	4	5
Total PCB Total	Data $\bar{x}$	43.1	26.4	25.6	18.1	16.2
	S_e	(6.09)	(1.69)	(6.09)	(1.96)	(3.47)
	Model $\bar{x}$	45.2	26.2	24.3	12.4	10.3
	% Error	4.9	1.5	5.1	31.5	36.4
Dissolved	Data $\bar{x}$	27.0	14.8	15.7	14.1	13.7
	S_e	(6.62)	(1.4)	(5.36)	(1.97)	(3.59)
	Model $\bar{x}$	22.5	14.8	12.6	10.5	8.9
	% Error	16.7	.7	19.7	25.5	35.0
Particulate	Data $\bar{x}$	16.2	11.6	9.91	3.98	2.57
	S_e	(1.82)	(1.17)	(1.11)	(.47)	(.31)
	Model $\bar{x}$	22.7	11.3	11.8	1.9	1.5
	% Error	40.1	2.6	19.1	52.3	41.6
Aroclor 1242 Total	Data $\bar{x}$	23.0	13.4	12.7	7.7	6.87
	S_e	(3.8)	(1.15)	(3.31)	(.75)	(1.67)
	Model $\bar{x}$	25.9	13.4	12.6	4.4	4.3
	% Error	12.6	0	.8	42.9	37.4

Dissolved	Data $\bar{x}$	15.6	8.09	8.13	5.95	5.83
	S_e	(3.72)	(.96)	(2.83)	(.73)	(1.70)
	Model $\bar{x}$	14.3	8.4	7.3	4.0	3.8
	% Error	9.1	3.8	10.2	32.8	34.8
Particulate	Data $\bar{x}$	7.45	5.31	4.52	1.71	1.04
	S_e	(.71)	(.56)	(.62)	(.23)	(.121)
	Model $\bar{x}$	11.6	5.0	5.3	.4	.43
	% Error	55.7	5.8	17.3	76.6	58.7
Aroclor 1260 Total	Data $\bar{x}$	20.1	12.8	12.8	10.4	9.36
	S_e		(1.69)	(2.88)	(1.45)	
	Model $\bar{x}$	19.3	12.2	11.7	7.9	6.1
	% Error	4.0	2.3	8.6	24.0	58.7
Dissolved	Data $\bar{x}$	11.4	6.68	7.45	8.13	7.83
	S_e		(.81)	(2.64)	(1.47)	
	Model $\bar{x}$	8.2	6.4	5.3	6.5	6.1
	% Error	28.1	4.2	28.9	20.0	34.8
Particulate	Data $\bar{x}$	8.7	6.34	5.39	2.27	1.53
	S_e		(.64)	(.57)	(.25)	
	Model $\bar{x}$	11.1	6.4	6.4	1.4	1.0
	% Error	27.6	.6	18.7	38.3	34.6

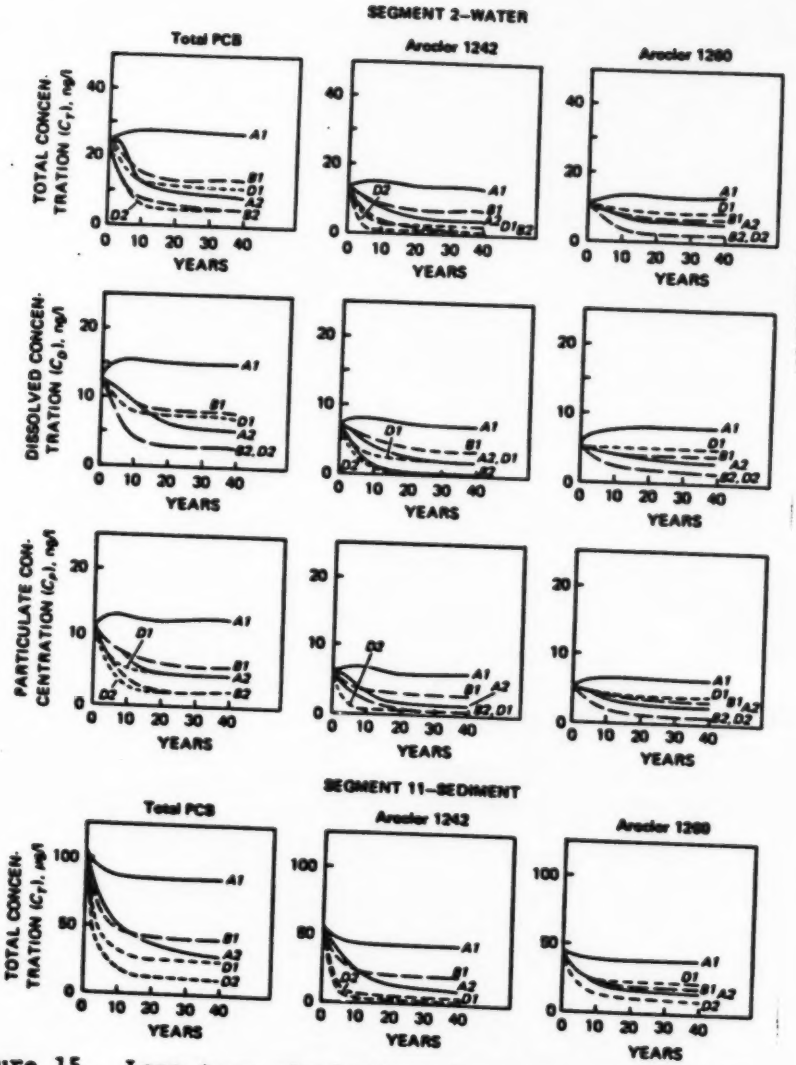


Figure 15. Long term simulation of average PCB concentrations in Saginaw Bay, segment 2. (See text for labels).

jected concentrations in segment 2 if the loads (Saginaw River and atmospheric) were reduced to zero. For comparison Simulations A and B with and without loads (1 and 2, respectively), are also shown in Figure 15. The difference between the total PCB model and the two-mixture model both calibrated with volatilization is indicated by B-1 and D-1. Therefore, it might be concluded that little was gained by the refinement of the model to include two mixtures. How-

ever, the two-mixture model has revealed the problem of calibrating A1242 and required the inclusion of a loss mechanism. Thus, the real difference between the modeling results would be represented by Simulation A-1, without volatilization calculated where concentrations actually increase slightly, and B-1, with volatilization.

CONCLUSIONS

PCB data collected in 1979 from Saginaw River and Bay have revealed differences in inputs, transport, and fate of two industrial mixtures, Aroclor 1242 and Aroclor 1260. Although the A1242 composes over 65% of the tributary load, its concentration is about equal to that of A1260 in the bay. This is partly due to the fact that atmospheric loads of A1242 are only 42% of the total but also due to the different partitioning with solids and different volatilization rates as revealed by use of a dynamic, mass balance model. The model included PCB-solids interaction, water-sediment interaction, and volatilization and was used to simulate 1979 PCB and solids concentrations. The best comparison of model simulations to the measured concentrations was made with the distribution coefficients for A1242 of about 60% of those for A1260 and with a volatilization rate for Aroclor 1242 of 0.2 m/day. The volatilization rate for A1260 was determined to be no more than 0.05 m/day. The calibrated volatilization rate for Aroclor 1242 compares well with that calculated from the theory described by O'Connor (0.21 m/day). In contrast, the calibrated volatilization rate for 1260 is much smaller than the theoretical (0.17). The reason for this disparity is not known.

The simulations of PCB also reveal the relative importance of each transport mechanism. In the inner bay for total PCB (the sum of A1242 and A1260), Saginaw River contributes 277 kg/yr whereas 226 in input from the atmosphere. A net mass of 689 kg is resuspended from the active sediment layer, 787 kg loss from volatilization and 417 kg transported to the outer bay. Twenty-eight kilograms are lost to the deep sediment. This all results in a loss of 12.2 kg from the water column and 717 kg from the active sediment during one year.

Long-term simulation indicate that if volatilization is occurring at the rates of 0.2 and 0.05 m/day for Aroclor 1242 and Aroclor 1260, respectively, total PCB in segment 2 will decrease about 50% within about 10 years. Most of this reduction, however, would be for Aroclor 1242 (80%). Aroclor 1260 would only decrease by about 20%. If all loads

were eliminated (Simulation D2, Figure 18), total PCB would decrease by 90% within 10 years. These conclusions depend on the validity of the volatilization process and the rationale for its inclusion. Confirmation should be done by conducting a similar monitoring effort of water and sediments in about five years to obtain verification data.

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